

Asian Journal of Environment & Ecology

Volume 23, Issue 5, Page 19-29, 2024; Article no.AJEE.114841 ISSN: 2456-690X

Human Health Risk Assessment of Some Trace Metals through Fish Consumption from Qua Iboe River, Oruk Anam, Nigeria

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Author's contribution

The sole author designed, analyzed, interpreted and prepared the manuscript.

Article Information

DOI: 10.9734/AJEE/2024/v23i5544

Open Peer Review History:

This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/114841

Original Research Article

Received: 13/01/2024 Accepted: 19/03/2024 Published: 26/03/2024

ABSTRACT

Food consumption is an important route of human exposure to organic chemicals. To assess the health risks associated with these chemicals due to fish consumption, the levels of trace metals (Cd, Cr, Ni, Cu, V, Pb and Sn) in water and fish from Qua Iboe River were assessed using atomic absorption spectrometry (ASS). Physicochemical parameters in water were determined using standard methods. The levels of physicochemical parameters in water were within permissible limits set by World Health Organisation (WHO). The levels of trace metals in water samples varied from one sampling location to another and ranged from 0.01 ± 0.01 to 0.10 ± 0.00 mg/L in wet season and from 0.01 ± 0.01 to 0.08 ± 0.01 mg/L in dry season. In fish, the levels ranged from 0.01 ± 0.01 to 0.61 0.01 mg/kg in wet season and from 0.02± 0.01 to 0.51± 0.01mg/kg in dry season. Results of physicochemical parameters showed variations across the sampling locations and seasons. Human health risk of trace metals contamination due to consumption of the fish revealed that hazard quotient (HQ) values were all less than unity (HQ <1). It therefore means that there is no health risk

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implication for consumers of commercial fish from the river. From the results, routine monitoring of these metals in studied river is strongly recommended to check escalation. Riverine communities should be educated by government on danger associated with indiscriminate disposal of wastes into aquatic environment.

Keywords: Trace metals; physicochemical; fish; analysis; statistical; Oruk Anam; Nigeria.

1. INTRODUCTION

Environmental sustainability is a major consideration in environmental management It is majorly achieved through routine monitoring to assess the levels of contaminants with a view to prevent escalation [1]. ''The process of monitoring the environment to evaluate the levels of some contaminants enables sustainability of the environment. ''Monitoring of environmental media including water and fish provides useful information on the pollution level of the aquatic environment and can provide a vital step in exposure control'' [8]. The analysis of aquatic biota such as fish gives information on the accumulation of contaminants and also on biomagnification in the food chain.

Assessment of human health risk of chemicals and chemical agents through researches is necessary for maintenance of sustainable environment for healthy living. ''Longer period of exposure of humans to contaminants such as trace metals, chemicals and chemical agents in the environment through oral intake can result in high risk to human health' [2]. ''Higher levels of chemical agents in water, food, air and soil are potentially harmful to humans as a result of exposure [3]. "There are so many sources of contaminants into water bodies. These include the following natural cycles such as carbon, nitrogen, water, oxygen" (Ikpe *et al.,* 2019). "Researches reveal that low levels of some trace metals are necessary for healthy growth of aquatic animals and may also become toxic at elevated levels in organs and tissues as a result accumulation and consequently can result in growth and reproduction impairment" [4].

"Aquatic organisms such as fish, among others have higher concentrations of trace metals than water as a result of accumulation making them more suitable for routine monitoring and also relevant in the exposure assessment of humans and wildlife" [5]. "Fish accumulates some trace metals in its fatty tissues due to its inability to metabolise them in the food they eat and from the intake of particulates in water and sediment unto which these chemicals have been adsorbed" (Gbeddy *et al.,* 2015). "The region of

accumulation of these metals within fish varies with the route of uptake. The gills are directly in contact with water, therefore the concentration of metals in gills reflects their concentration in water where the fish live" [6]. "The concentration of these trace metals increases proportionately across a food chain. The bioaccumulation of trace metals in fish and other animals is main source of human daily intake of such chemicals other than from water" [7].

"The potential use of fish as bio-monitors for assessment of bioaccumulation and biomagnification of contaminants in aquatic environment is significant as a result of bioaccumulation" (Ikpe *et al.,* 2019)*.*

Possible sources of trace metals into rivers abound. These include urban activities within the area of study. ''The presence of such foreign chemicals in the river, could readily affect the vital fish population among others. This is because fish has the tendency to bioaccumulate these hydrophobic chemicals in its tissues and organs and is a suitable indicator for environmental pollution monitoring'' (Udosen *et al.,* 2012).

According to Ubong *et al.* (2023) "the exposure assessment is a function of quantitative determination of the extent of exposure of the population to the hazardous agent. The assessment gives the real knowledge of the state of pollution of an area and dates obtained in environmental monitoring are commonly used as a starting point. Characterisation of risk takes into consideration the consequences of exposure to chemical contaminants in the environment. It gives the basis of the validity of the result".

Water bodies are continually polluted with trace metals and other chemical agents due to anthropogenic activities and natural processes. ''Of certainty is the fact that when it rains, trace metals are washed into the aquatic environment, and due to their low solubility in water, they become strongly bonded to particulate matter in aquatic sediment and in turn become available to biota such as fish and humans that eat the fish'' [8]. ''Though trace metals are usually present in water at low levels, aquatic organisms have been shown to accumulate them in their tissues and also transfer to secondary feeders. Since water, sediment and fish are the ultimate reservoirs of these chemicals, they often accumulate them in such a way that can cause health problems such as kidney and liver damage, central nervous system damage, thyroid and bladder damage as well as kidney and liver cancer in animals that depend directly or indirectly on the fish and the water bodies'' [10]. "In recent times, Oruk Anam has witnessed tremendous anthropogenic activities culminating in the overall development of the area. These activities include roads construction, industrialisation transportation of all kinds and all forms of agricultural practices. The end products and the after effects of all these activities are usually washed into the aquatic environment when it rains, polluting the ecosystem with all kinds of trace metals. Many studies have been carried out on the concentration of trace metals in different portions of Qua Iboe River" [3]. However, information on the emerging trends of these chemicals in Qua Iboe River, Oruk Anam, especially the information on fish samples are non-existent, therefore, there is every need to quantify the levels of trace metals in fish from Qua Iboe River, Oruk Anam and also to assess the health risk on humans associated with the consumption of the fish.

1.1 Quality Control and Assurance

The implementation of laboratory quality assurance and quality laboratory methods, including the use of standard operating procedures, calibrations with standards, analysis of reagent blanks and analysis of replicates guaranteed the quality of the analytical data. Each sample was analysed in triplicates. All chemicals and reagents used in the study were of analytical grade. Standard solutions prepared were performed under clean laboratory environment. All samples were digested alongside with blanks.

1.2 Statistical Analysis

The generated data were processed using the statistical package for social sciences (SPSS).

2. MATERIALS AND METHODS

2.1 Study Area

The area of this study is Qua Iboe River (QIR), Oruk Anam, Nigeria. The Map of the study area is located between latitude 04° 28'31.0'N and 07° $10'12.4'$ N and longitude $06°65'41.2'E$ and $06°52'$ 50.5'E of Greenwich Meridian. The river flows from Etim Ekpo through Ikot Okoro in Oruk Anam via Ibagwa in Abak to Ekpene Obom and Ekpene Ukpa in Etinan Local Government Area, then through Ndiya in Nsit Ubium local government area before flowing into Alantic Ocean via Beight of Bonny [9]. It is one of the major sources of water for the inhabitants of these local government areas. The distances between sampling locations were about 200 meters apart. The sampling locations in this study as contained in the map of the study area were:

2.2 Samples Collection and Preservation

Samples were collected between November and October covering wet and dry seasons from the five sampling stations namely: Inen Nsai, Umani, Ikot Okoro, Nung Ikot and Ibesit using Inen Nsai as a control station.

Water samples: The bottles were pre-rinsed several times with the water from the different sampling locations. Water samples were collected according to Udosen *et al.* [4] by dipping each mouth of the container against the flow direction to avoid trapping air bubbles in the bottle. Water samples were collected using prerinsed 1-litre (1L) polyethylene bottles with caps for the analysis of water quality parameters. Water samples for dissolved oxygen determination were fixed on site with 2 mL of Winkler solutions 1 and 11. The samples for trace metals analysis were collected with $HNO₃$ pre-rinsed (1L) polyethylene containers and 5 mL of concentrated nitric acid $(HNO₃)$ to a pH < 2 was added to maintain the oxidation state of the metals and to reduce microbial action. The samples collected were transported to the laboratory and preserved in a refrigerator to 4°C [2].

Fish samples: Fish samples were collected from the local fishermen fishing in the river using local fishing traps (Ikpa) set adjacent to the sampling locations at dusk and inspected at dawn [9]. Five medium sized fish samples were obtained very early in the morning and were put in a locally made aquarium and transported immediately to laboratory for further analysis [3]. Prior to analysis, the fish samples were washed with distilled water to remove loosely held particles before they were gutted and decapitated using stainless steel kitchen knife. The decapitated fish samples were filleted on both sides, placed in a porcelain crucible and dried in an oven. The dried muscles were homogenized using mortar and pestle. The resultant homogenized fish samples were stored in a well-labeled plastic bag before digestion.

2.3 Determination of Trace Metals in Water

The concentrations of trace metals were determined using UNICAM solar 969 Atomic Absorption Spectrophotometer (AAS). The water

samples (100 mL each) were filtered using filter paper No.1. The filtrate was acidified with $HNO₃$ (10 mL) and 50% HCl solution (10 mL). It was evaporated to near dryness on an electric hot plate. The solution was transferred to a 100 mL volumetric flask and made up to mark with deionized water. A blank was also prepared the same way with the omission of the sample using deionized water. The samples were aspirated into the air/acetylene flame.

Fig. 1. Map of study area

2.4 Determination of Trace Metals in Fish

Fish samples from each sampling location were dried in an oven at 80° C for 24 hours after which they were homogenized to powder form. Exactly 2 g of each were weighed and transferred to a beaker. Into each of the beakers, trioxonitrate (v) acid (6 mL) and perchloric acid (2 mL) were added and stirred. Distilled water (30 mL) was also added. Each beaker was placed on the hot plate and heated for digestion to take place. After heating, the samples were allowed to cool, filtered and the volume was made up to 50 mL using deionized water. Then the digested samples were used for the analysis. The digests were prepared in triplicates and a blank determination was also made using 25 mL volumetric flask and made up to the mark with distilled water. These geochemical fractions were analysed using Atomic Absorption spectrophotometer (Ikpe *et al.,* 2019).

2.5 Human Health Risk Assessment of Trace Metals Through Fish Consumption

The exposure assessment via consumption of fish was evaluated using Equations 1 and 2.

$$
\text{Intake }_{\text{(seafood)}}\left(\text{mg/kg/day}\right)=\frac{\text{(CF x IR x FL x EP x ED)}}{\text{(BW x AT)}}\text{ (1)}
$$

$$
HQ = \frac{\text{Intake}}{\text{RfDo}}\tag{2}
$$

Here, CF is the chemical concentration in fish(mg/kg), IR is ingestion rate (kg/day), FI is the fraction ingested (unitless), ED is exposure duration, EF is exposure frequency (365 days/year), BW is body weight and AT is the averaging time (period over which exposure is average in days). RfDo is the oral reference doses of the trace metals. The actual risk was characterized based on hazard quotient (HQ) as shown in equations 1 and 2. HQ below one (1) implies that the level of exposure is not likely to cause any obvious adverse effects (Gbeddy *et al.*, 2015; Emarah *et al.,* 2015; Krishna *et al.,* [10]. Alino and Alajoa, [11] Uwah et al. [12].

2.6 Quality Assurance

The implementation of laboratory quality assurance and quality laboratory methods, including the use of standard operating procedures among others guaranteed the quality of the analytical data [5].

2.7 Statistical Analysis

The generated data were processed using the statistical package for social sciences (SPSS).

3. RESULTS AND DISCUSSION

The results of analysis of trace metals in fish and physicochemical parameters from five sampling locations are discussed in this unit. Table .1 shows the levels of physicochemical parameters in surface water in wet and dry seasons; Table 2 shows the levels of trace metals in water in wet and dry seasons; Table 3 shows the levels of trace metals in fish in both wet and dry seasons; Tables 4 shows estimated risk (in terms of HQ) of trace metals via fish consumption.

3.1 Physicochemical Parameters

The results of the physiochemical parameters in water are presented in Tables 1 are discussed in this section. The determination of level of physicochemical parameters of an aquatic environment is imperative before pollution study is carried out. For instance thermal pollution can lead to a negative impact on the aquatic environment. Some aquatic organisms are adapted to survive within a specific temperature range. Increase in temperature can cause cold water species to be replaced by warm water species. In addition, increase in thermal pollution can lead to increase in vulnerability of fish to toxic compounds, parasites and disease [13]. Temperatures reaching extremes of heat or cold in aquatic environment could lead to survival of only a few organisms. Depletion of dissolved oxygen (DO) can lead to extinction of aquatic organisms [12].

Temperature: The temperature of the water samples ranged between 27.0 and 30.0° C across the sampling locations with a mean of 29.2± 0.49 for wet season and between 29.0 and 32.0° C with a mean of 30.3 ± 0.24 for dry season.

Hydrogen Ion (pH): Hydrogen ion concentration of surface water in this study ranged between 6.3 and 6.9 with the mean of 6.5 ± 0.5 during the wet season while it ranged between 7.1 and 7.4 during the dry season with the mean of $7.2_±$ 0.06.

Total Dissolved Solids (TDS): The TDS levels in water in the wet season ranged between 70.50 and 97.73 mg/L with mean level of 87.08± 0.02 mg/L while the range in dry season was between 86.00 and 124.00 mg/L with a mean level of 87.08 ± 0.02 mg/L. These levels were similar to levels reported by Iqbal and Shah [14].

Total Suspended Solids (TSS): The levels of total suspended solids in water samples obtained in this study ranged between 56.16 and 81.60 mg/L in wet season with mean level of $72.19 \pm$ 9.29 mg/L and between 103.00 and 136.33 mg/L during dry season with mean level of 120.93±13.40 mg/L.

Electrical Conductivity (EC): Electrical conductivity also called specific conductance is the capacity of water to conduct electricity and varies both with the number and types of ions the solution contains. It is also a temperaturedependent parameter [4,2]. Electrical conductivity of the water samples ranged between 110.40 and 123.36µS/cm in wet season with a mean level of 118.74 \pm 2.24 μ S/cm and ranged between 132.70 and 167.67 µS/cm during the dry season with a mean level of 149.21±15.57 µS/cm.

Dissolved Oxygen (DO): The levels of DO in water samples across the sampling locations ranged between 6.10 and 11.50 mg/L with a mean level of 8.53 ± 0.17 mg/L in the wet season and during dry season, the levels ranged between 5.53 and 10.40 mg/L with a mean level of 7.74±0.26 mg/L. These results were similar to results reported by Inam *et al.,* [15].

Biochemical Oxygen Demand (BOD): The levels of BOD in surface water samples in this study ranged between 2.05 and 4.50 mg/L with mean level of 3.06 ± 0.01 mg/L during wet season and ranged between 2.03 and 4.01 mg/L with mean level of 2.92±0.01 mg/L in dry season.

Chloride: Chloride levels in surface water ranged between 19.01 and 35.20 mg/L in wet season and between 18.20 and 34.60 mg/L during dry season with mean levels of 24.41±1.04 mg/L and 23.20±5.06 mg/L in wet and dry seasons respectively.

Nitrate: Nitrate levels in surface water in this study ranged between 1.26 and 1.74 mg/L in wet season and between 1.32 to 2.04 mg/L in dry season with mean levels of 1.52±0.20 mg/L and 1.61±0.31 mg/L for wet and dry seasons respectively.

Sulphate: Sulphate levels in surface water in this study ranged between 5.01 and 5.29 mg/L in the wet season with mean levels of 5.18±0.12 mg/L. During the dry season, the levels ranged

between 5.18 and 6.15 mg/L with mean levels of 5.20±0.55 mg/L

Phosphate: Phosphate levels in surface water ranged between 0.22 and 0.31 mg/L during wet season and 0.23 to 0.33 mg/L in the dry season with mean levels of 0.25±0.25 and 0.28±0.10 mg/L for wet and dry seasons respectively.

Nitrite: Nitrite levels in surface water in this study ranged between 0.01 and 0.05 mg/L with a mean value of 0.02±0.14 mg/L in wet season and 0.02 mg/L in all locations with mean level of 0.02±0.01 mg/L during dry season.

Turbidity: Turbidity levels in surface water ranged between 1.52 and 2.76 NTU with mean level of 1.85±0.01 NTU in wet season and between 1.51 and 2.72 NTU with mean level of 1.80±0.01 NTU for dry season

3.2 Levels of Trace Metals in Surface Water

Table 2 shows the levels of trace metals in water in both wet and dry seasons. The distribution pattern of the levels of trace metals in surface water indicates $Cu > Cd > Cr > V > Ni > Sn > Pb$.

Levels of Cadmium: The levels of cadmuim in water samples across sampling locations during wet season ranged between 0.02±0.01 and 0.05±0.01 mg/L and between 0.03±0.01 and 0.080±0.01 mg/L during dry season.

Levels of Chromium: The levels of Cr in surface water ranged between 0.01±0.01 and 0.068±0.01 mg/L in wet season and during dry season, the levels ranged between 0.02±0.09 and 0.087±0.004 mg/L.

Levels of Nickel: The levels of Ni across sampling locations ranged between 0.01±0.01 and 0.03±0.01 mg/L in wet season and between 0.02±0.01 and 0.04± 0.00 mg/L during dry season.

Levels of Copper: The mean levels of Cu in surface water across sampling locations during wet season ranged between 0.02±0.01 and 0.08±0.01 mg/L in wet season and between 0.03±0.01 and 0.10±0.01 mg/L during dry season. These results were similar to levels reported by Benson *et al.,* [16].

Levels of Vanadium: The mean levels of V in surface water across all sampling locations during wet season ranged from 0.01±0.01 to 0.03± 0.01 mg/L and from 0.02±0.01 to 0.04±0.01 mg/L.

Sampling Locations		Temp (°C)	рH	TDS (mg/L)	EC $(\mu s/cm)$	DO (mg/L)	BOD (mg/L)	CI ⁻ (mg/L)	NO ₃ (mg/L)	SO_4^{2-} (mg/L)	PO ₄ 3 (mg/L)	NO ₂ (mg/L)	Salinity (mg/L)	
	Wet	27.01	6.50	70.50	119.13	6.13	2.05	19.01	1.32	5.13	0.23	0.01	1.52	
	Dry	29.01	7.20	86.00	133.33	5.53	2.04	18.20	1.32	5.18	0.23	0.02	1.51	
UM	Wet	29.02	6.20	73.50	110.40	6.10	2.60	19.43	1.26	5.01	0.22	0.02	1.56	
	Dry	29.67	7.13	92.67	132.70	6.80	2.50	18.41	1.45	5.91	0.23	0.02	1.53	
	Wet	30.08	6.80	96.80	119.63	8.90	3.09	21.92	1.63	5.23	0.24	0.02	1.71	
	Drv	30.90	7.30	107.00	145.00	7.30	3.02	19.50	. 85. ،	6.05	0.30	0.02	1.63	
ΝI	Wet	30.10	6.30	96.88	121.18	10.01	3.10	26.50	1.67	5.26	0.26	0.02	1.73	
	Dry	30.01	7.40	123.00	167.33	9.50	3.05	25.30	1.97	6.14	0.32	0.02	1.65	
IB	Wet	30.02	6.40	97.73	123.36	11.50	4.50	35.20	1.74	5.29	0.31	0.05	2.76	
	Dry	32.11	7.41	124.00	167.67	10.40	4.01	34.60	2.04	6.15	0.33	0.02	2.72	

Table 1. Levels of physicochemical parameters in surface water from the sampling locations for wet and dry seasons

IN = Inen Nsai, UM = Umani, IO = Ikot Okoro, NI = Nung Ikot, IB = Ibesit, STD = Standard Deviation

Table 2. Levels (mg/L) of trace metals in surface water of Qua Iboe River for wet and dry seasons

Within column, different superscript letters mean significantly different (p<.05).

Table 4: Risks assessment in terms of hazard quotient (HQ) of trace metals via fish consumption

Levels of Lead: The levels of Pb in water across sampling locations ranged between 0.00±0.00 and 0.01± 0.00 mg/L in wet season and between 0.00±0.00 and 0.01±0.00 mg/L during dry season.

Levels of Tin: The mean levels of Sn in water across sampling locations ranged between 0.00±0.01 and 0.02±0.01 mg/L in wet season and during dry season levels obtain ranged between 0.02±0.00 to 0.03±0.01 mg/L. Exposure to high levels of inorganic tin may cause symptoms including stomach aches, liver and kidney problems, and anemia [7].

3.3 Levels of Trace Metals in Fish

The levels of trace metals obtained in fish varied across the seasons as presented in Table 3. The distribution pattern was Cu > Cd > Cr > Sn > Ni > V > Pb. The level of Cu recorded was highest compared to other trace metals studied [17].

Levels of Cadmium: The levels of Cd in fish across the sampling locations ranged between 0.06±0.01 and 0.78±0.01 mg/kg in wet season and between 0.90 ± 0.00 and 0.73 ± 0.01 mg/kg during dry season.

Levels of Chromium: The levels of Cr in fish ranged between 0.87±0.02 and 0.87±0.01 mg/kg during wet season and between 0.74±0.00 and 0.71±0.01 mg/kg in dry season.

Levels of Nickel: The levels of Ni in fish ranged between 0.93±0.01 and 0.03±0.01 mg/kg in wet season while in dry season the levels ranged between 0.76±0.00 and 0.91±0.01 mg/kg.

Level of copper: The levels of Cu in fish ranged between 1.06±0.01 and 14.98±0.01 mg/kg in wet season and between 2.93±0.01 and 16.54±0.001 mg/kg in dry season.

Levels of Vanadium: The levels of V obtained in fish samples in this study ranged between 0.63±0.01 and 5.56±0.01 mg/kg in wet season and between 0.93±0.01 and 5.43±0.020 mg/kg during dry season.

Levels of Lead: The levels of Pb in fish in the study during wet season ranged between 0.01±0.01 and 0.98±0.01 mg/kg while in dry season the range was between 0.12±0.00 and 0.98±0.01 mg/kg.

Levels of Tin: The levels of Sn obtained in fish across all the sample locations ranged between 0.67±0.01 and 4.56 mg/kg in wet season and between 0.76 ± 0.01 and 5.43 ± 0.01 mg/kg during dry season. Highest mean level of tin 5.43 \pm 0.01 mg/kg was obtained at Ibesit sampling location [18].

3.4 Human Health Risk of Trace Metals Via Fish Consumption

Calculation of exposure (due to oral intake) of trace metals through fish consumption from Qua Iboe River are presented in Table 4. The result revealed the following trends of exposures across all locations and seasons: Cu > Cd > Cr > $Ni > V > Sn > Pb$. Also revealed was that levels were higher though not significantly around Ibesit, Nung Ikot and Ikot Okoro (downstream) compared to Umani and Inen Nsai due to intense anthropogenic activities downstream. The estimated risks of trace metals via fish consumption from the studied river as presented in Table 4 indicated no risk as hazard quotients for the metals determined in fish were less than unity (HQ <1) across all the sampling locations. It therefore means that there is no health risk implication for consumers of commercial fish from the river.

4. CONCLUSION

The following conclusions were drawn based on the statistical analyses of the results. The water and fish samples obtained from the five sampling locations of Qua Iboe River contain variable levels of the investigable parameters. The investigated parameters show seasonal variations in the samples. Correlation analysis revealed positive relationships between Cd with Cr, Ni, Cu, V and Pb in the water, fish and sediment in both the dry and wet seasons. There were also positive relationship between the trace metals in water and sediment, water and fish as well as sediment and fish in the two seasons. The levels of physicochemical parameters of the water and sediment were all within permissible limits set by WHO, FEPA and NIS. The levels of Cd, Cr, Ni, V, Pb and Sn in the water were all within WHO and NIS guidelines except for copper.

Risk assessment of the trace metals through fish consumption from the studied river indicated low risk.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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